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(54) Title: FOAM DYE COMPOSITION COMPRISING AT LEAST TWO DIOL COMPOUNDS EACH COMPRISING AT LEAST 4 CARBON ATOMS

(57) Abstract: The invention relates to a composition for dyeing human keratin fibres such as the hair, in foam form, comprising at least one alkaline agent, at least one oxidizing agent, at least one oxidation dye precursor and at least two diol compounds each comprising at least 4 carbon atoms selected from dipropylene glycol, diethylene glycol and hexylene glycol. The invention also relates to a process for dyeing human keratin fibres using this composition. A subject of the invention is also a device for dyeing keratin fibres, comprising the composition of the invention in liquid form and a foam dispenser for delivering the composition in the form of a foam.



## FOAM DYE COMPOSITION COMPRISING AT LEAST TWO DIOL COMPOUNDS EACH COMPRISING AT LEAST 4 CARBON ATOMS

The present invention relates to a dye composition in foam form.

Among the methods for dyeing human keratin fibres, such as the hair, mention  
5 may be made of oxidation dyeing or permanent dyeing. More particularly, this form of dyeing uses one or more oxidation dyes, usually one or more oxidation bases optionally combined with one or more couplers.

In general, oxidation bases are chosen from ortho- or para-phenylenediamines, ortho- or para-aminophenols and heterocyclic compounds. These oxidation bases are  
10 colourless or weakly coloured compounds which, when combined with oxidizing products, can give access to coloured entities.

The shades obtained with these oxidation bases are often varied by combining them with one or more couplers, these couplers being chosen especially from aromatic meta-diamines, meta-aminophenols, meta-diphenols and certain  
15 heterocyclic compounds, such as indole compounds.

The variety of molecules used as oxidation bases and couplers allows a wide range of colors to be obtained.

Permanent dyeing processes thus consist in using, with the dye composition, an aqueous composition comprising at least one oxidizing agent, such as hydrogen  
20 peroxide, under alkaline pH conditions in the vast majority of cases. The alkaline agent conventionally used is aqueous ammonia or other alkaline agents, such as alkanolamines.

Dye compositions may take various forms such as lotions, gels, emulsions, creams or foams. Dyeing foams are pleasant to use, however they often exhibit a  
25 poor staying power over time. For example, it is possible to observe a rapid disappearance of the foam after application or a non-uniform application along the fibres.

There is a real, constant need to develop oxidation dye compositions in foam form that are easy to prepare and to apply, and which remain sufficiently stable over  
30 time while retaining efficient dyeing properties.

This aim and others are achieved by the present invention, one subject of which is thus a composition for dyeing keratin fibres such as the hair, in foam form, comprising at least one alkaline agent, at least one oxidizing agent, at least one oxidation dye precursor and at least two diol compounds comprising at least 4 carbon  
35 atoms selected from dipropylene glycol, diethylene glycol and hexylene glycol.

The invention also relates to a process for dyeing human keratin fibres using this composition.

A subject of the invention is similarly a multi-compartment device comprising, in a first compartment, a first composition containing at least one oxidation dye

precursor, at least one alkaline agent and at least two diol compounds comprising at least 4 carbon atoms selected from dipropylene glycol, diethylene glycol and hexylene glycol ; in a second compartment, a second composition containing one or more oxidizing agents, one of the two compartments being equipped with a component for delivering the composition of the invention in foam form after mixing with the other composition, or the component for delivering the composition in foam form is included in a third compartment.

A subject of the invention is also a device for dyeing keratin fibres, comprising the composition of the invention in liquid form and a foam dispenser for delivering the composition in the form of a foam.

The composition of the invention is in the form of a foam that is particularly pleasant to apply. It has a light, airy texture, which makes it particularly pleasant to use. The qualities of the foam are sufficiently long-lasting to enable uniform application of the dye product, without running. The composition of the invention makes it possible to obtain improved dyeing properties, such as strength of the colour, resistance to external agents (shampooing, perspiration, light) and selectivity, which are particularly efficient.

Other features and advantages of the invention will become more clearly apparent on reading the description and the examples that follow.

In the text hereinbelow, unless otherwise indicated, the limits of a range of values are included in that range. The expression "at least one" is equivalent to the expression "one or more".

According to one particular embodiment, the two diol compounds are dipropylene glycol and hexylene glycol.

The amount of diol compound(s) comprising more than 4 carbon atoms as defined in the invention may range from 0.1% to 30%, preferably from 0.5% to 20% and better still from 1% to 10% by weight of the total weight of the composition.

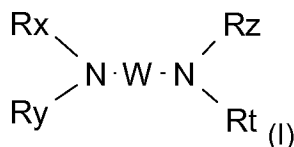
The composition in foam form according to the invention comprises at least one alkaline agent. This agent may be chosen from mineral or organic or hybrid alkaline agents, or mixtures thereof.

The mineral alkaline agent(s) are preferably chosen from aqueous ammonia, alkali carbonates or bicarbonates such as sodium or potassium carbonates and sodium or potassium bicarbonates, sodium hydroxide or potassium hydroxide, or mixtures thereof.

The organic alkaline agent(s) are preferably chosen from organic amines with a  $pK_b$  at 25°C of less than 12, preferably less than 10 and even more advantageously less than 6. It should be noted that it is the  $pK_b$  corresponding to the function of highest basicity.

Hybrid compounds that may be mentioned include the salts of the amines mentioned previously with acids such as carbonic acid or hydrochloric acid.

The organic alkaline agent(s) are chosen, for example, from alkanolamines, oxyethylenated and/or oxypropylenated ethylenediamines, amino acids and the compounds of formula (I) below:



in which W is a C<sub>1</sub>-C<sub>6</sub> alkylene residue optionally substituted with a hydroxyl group or a C<sub>1</sub>-C<sub>6</sub> alkyl radical; Rx, Ry, Rz and Rt, which may be identical or different, represent a hydrogen atom or a C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>1</sub>-C<sub>6</sub> hydroxyalkyl or C<sub>1</sub>-C<sub>6</sub> aminoalkyl radical.

Examples of such amines that may be mentioned include 1,3-diaminopropane, 1,3-diamino-2-propanol, spermine and spermidine.

The term "alkanolamine" means an organic amine comprising a primary, secondary or tertiary amine function, and one or more linear or branched C<sub>1</sub>-C<sub>8</sub> alkyl groups bearing one or more hydroxyl radicals.

Alkanolamines such as monoalkanolamines, dialkanolamines or trialkanolamines comprising from one to three identical or different C<sub>1</sub>-C<sub>4</sub> hydroxyalkyl radicals are in particular suitable for performing the invention.

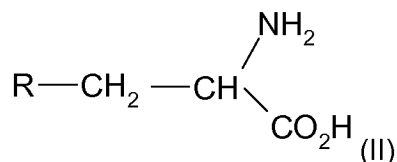
Among compounds of this type, mention may be made of monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, diisopropanolamine, N-dimethylaminoethanolamine, 2-amino-2-methyl-1-propanol, triisopropanolamine, 2-amino-2-methyl-1,3-propanediol, 3-amino-1,2-propanediol, 3-dimethylamino-1,2-propanediol and tris(hydroxymethylamino)methane.

More particularly, the amino acids that can be used are of natural or synthetic origin, in their L, D or racemic form, and comprise at least one acid function chosen more particularly from carboxylic acid, sulfonic acid, phosphonic acid or phosphoric acid functions. The amino acids may be in neutral or ionic form.

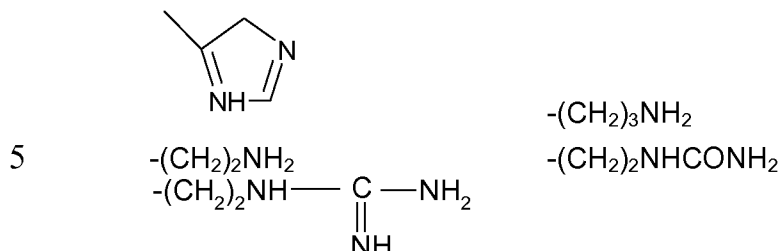
As amino acids that can be used in the present invention, mention may be made especially of aspartic acid, glutamic acid, alanine, arginine, ornithine, citrulline, asparagine, carnitine, cysteine, glutamine, glycine, histidine, lysine, isoleucine, leucine, methionine, N-phenylalanine, proline, serine, taurine, threonine, tryptophan, tyrosine and valine.

Advantageously, the amino acids are basic amino acids comprising an additional amine function optionally included in a ring or in a ureido function.

Such basic amino acids are preferably chosen from those corresponding to formula (II) below:



in which R denotes a group chosen from:



The compounds corresponding to formula (II) are histidine, lysine, arginine, ornithine and citrulline.

10 The organic amine may also be chosen from organic amines of heterocyclic type. Besides histidine that has already been mentioned in the amino acids, mention may be made in particular of pyridine, piperidine, imidazole, triazole, tetrazole and benzimidazole.

15 The organic amine may also be chosen from amino acid dipeptides. As amino acid dipeptides that can be used in the present invention, mention may be made especially of carnosine, anserine and baleine.

20 The organic amine is chosen from compounds comprising a guanidine function. As amines of this type that may be used in the present invention, besides arginine, which has already been mentioned as an amino acid, mention may be made especially of creatine, creatinine, 1,1-dimethylguanidine, 1,1-diethylguanidine, glycoamine, metformin, agmatine, N-amidinoalanine, 3-guanidinopropionic acid, 4-guanidinobutyric acid and 2-([amino(imino)methyl]amino)ethane-1-sulfonic acid.

Mention may be made in particular of the use of guanidine carbonate or monoethanolamine hydrochloride as hybrid compounds.

25 According to one particular embodiment, the composition of the invention comprises, as alkaline agent, one or more alkanolamines.

Preferably, the alkanolamine is monoethanolamine.

30 In one variant of the invention, the composition of the invention comprises, as alkaline agent, one or more alkanolamines, preferably monoethanolamine, and aqueous ammonia. In this variant, the alkanolamine(s) are present in a predominant amount relative to the aqueous ammonia, the content of the latter being expressed as ammonia.

Advantageously, the composition according to the invention has a content of alkaline agent(s) ranging from 0.01% to 30% by weight, preferably from 0.1% to 20% by weight and better still from 1% to 10% by weight relative to the weight of the said composition.

5 The composition according to the invention also comprises at least one oxidizing agent.

The oxidizing agents are chosen, for example, from hydrogen peroxide, urea peroxide, alkali metal bromates or ferricyanides, peroxygenated salts, for instance persulfates, perborates, peracids and precursors thereof and percarbonates of alkali  
10 metals or of alkaline-earth metals. Advantageously, the oxidizing agent is hydrogen peroxide.

The content of oxidizing agent(s) more particularly represents from 0.1% to 20% by weight and preferably from 0.5% to 10% by weight relative to the weight of the composition.

15 As indicated previously, the composition according to the invention comprises one or more oxidation dye precursors.

Oxidation bases and couplers may be used as oxidation dye precursors.

By way of example, the oxidation bases are chosen from para-phenylenediamines, bis(phenyl)alkylenediamines, para-aminophenols, ortho-aminophenols and heterocyclic bases, and the addition salts thereof.  
20

Among the *para*-phenylenediamines that may be mentioned, for example, are *para*-phenylenediamine, *para*-toluenediamine, 2-chloro-*para*-phenylenediamine, 2,3-dimethyl-*para*-phenylenediamine, 2,6-dimethyl-*para*-phenylenediamine, 2,6-diethyl-*para*-phenylenediamine, 2,5-dimethyl-*para*-phenylenediamine, N,N-dimethyl-*para*-phenylenediamine, N,N-diethyl-*para*-phenylenediamine, N,N-dipropyl-*para*-phenylenediamine, 4-amino-N,N-diethyl-3-methylaniline, N,N-bis( $\beta$ -hydroxyethyl)-*para*-phenylenediamine, 4-N,N-bis( $\beta$ -hydroxyethyl)amino-2-methylaniline, 4-N,N-bis( $\beta$ -hydroxyethyl)amino-2-chloroaniline, 2- $\beta$ -hydroxyethyl-*para*-phenylenediamine, 2-fluoro-*para*-phenylenediamine, 2-isopropyl-*para*-phenylenediamine, N-( $\beta$ -hydroxypropyl)-*para*-phenylenediamine, 2-hydroxymethyl-*para*-phenylenediamine, N,N-dimethyl-3-methyl-*para*-phenylenediamine, N-ethyl-N-( $\beta$ -hydroxyethyl)-*para*-phenylenediamine, N-( $\beta,\gamma$ -dihydroxypropyl)-*para*-phenylenediamine, N-(4'-aminophenyl)-*para*-phenylenediamine, N-phenyl-*para*-phenylenediamine, 2- $\beta$ -hydroxyethyloxy-*para*-phenylenediamine, 2- $\beta$ -acetylaminoethyloxy-*para*-phenylenediamine, N-( $\beta$ -methoxyethyl)-*para*-phenylenediamine, 4-aminophenylpyrrolidine, 2-thienyl-*para*-phenylenediamine, 2- $\beta$ -hydroxyethylamino-5-aminotoluene, 3-hydroxy-1-(4'-aminophenyl)pyrrolidine, and the addition salts thereof with an acid.  
35

Among the para-phenylenediamines mentioned above, para-phenylenediamine, para-toluenediamine, 2-isopropyl-para-phenylenediamine, 2- $\beta$ -hydroxyethyl-para-phenylenediamine, 2- $\beta$ -hydroxyethyloxy-para-phenylenediamine, 2,6-dimethyl-para-phenylenediamine, 2,6-diethyl-para-phenylenediamine, 2,3-dimethyl-para-phenylenediamine, N,N-bis( $\beta$ -hydroxyethyl)-para-phenylenediamine, 2-chloro-para-phenylenediamine and 2- $\beta$ -acetylaminoethyloxy-para-phenylenediamine, and the addition salts thereof with an acid, are particularly preferred.

Among the bis(phenyl)alkylenediamines that may be mentioned, for example, are N,N'-bis( $\beta$ -hydroxyethyl)-N,N'-bis(4'-aminophenyl)-1,3-diaminopropanol, N,N'-bis( $\beta$ -hydroxyethyl)-N,N'-bis(4'-aminophenyl)ethylenediamine, N,N'-bis(4'-aminophenyl)tetramethylenediamine, N,N'-bis( $\beta$ -hydroxyethyl)-N,N'-bis(4'-aminophenyl)tetramethylenediamine, N,N'-bis(4'-methylaminophenyl)tetramethylenediamine, N,N'-bis(ethyl)-N,N'-bis(4'-amino-3'-methylphenyl)ethylenediamine and 1,8-bis(2,5-diaminophenoxy)-3,6-dioxaoctane, and the addition salts thereof.

Among the para-aminophenols that may be mentioned, for example, are para-aminophenol, 4-amino-3-methylphenol, 4-amino-3-fluorophenol, 4-amino-3-chlorophenol, 4-amino-3-hydroxymethylphenol, 4-amino-2-methylphenol, 4-amino-2-hydroxymethylphenol, 4-amino-2-methoxymethylphenol, 4-amino-2-aminomethylphenol, 4-amino-2-( $\beta$ -hydroxyethylaminomethyl)phenol and 4-amino-2-fluorophenol, and the addition salts thereof with an acid.

Among the ortho-aminophenols that may be mentioned, for example, are 2-aminophenol, 2-amino-5-methylphenol, 2-amino-6-methylphenol and 5-acetamido-2-aminophenol, and the addition salts thereof.

Among the heterocyclic bases, mention may be made, by way of example, of pyridine derivatives, pyrimidine derivatives and pyrazole derivatives.

Among the pyridine derivatives that may be mentioned are the compounds described, for example, in patents GB 1 026 978 and GB 1 153 196, for instance 2,5-diaminopyridine, 2-(4-methoxyphenyl)amino-3-aminopyridine and 3,4-diaminopyridine, and the addition salts thereof.

Other pyridine oxidation bases of use in the present invention are the 3-aminopyrazolo[1,5-a]pyridine oxidation bases or the addition salts thereof described, for example, in Patent Application FR 2 801 308. Examples that may be mentioned include pyrazolo[1,5-a]pyrid-3-ylamine, 2-acetylamino pyrazolo[1,5-a]pyrid-3-ylamine, 2-(morpholin-4-yl)pyrazolo[1,5-a]pyrid-3-ylamine, 3-aminopyrazolo[1,5-a]pyridine-2-carboxylic acid, 2-methoxypyrazolo[1,5-a]pyrid-3-ylamine, (3-aminopyrazolo[1,5-a]pyrid-7-yl)methanol, 2-(3-aminopyrazolo[1,5-a]pyrid-5-yl)ethanol, 2-(3-aminopyrazolo[1,5-a]pyrid-7-yl)ethanol, (3-aminopyrazolo[1,5-a]pyrid-2-yl)methanol,

3,6-diaminopyrazolo[1,5-a]pyridine, 3,4-diaminopyrazolo[1,5-a]pyridine, pyrazolo[1,5-a]pyridine-3,7-diamine, 7-(morpholin-4-yl)pyrazolo[1,5-a]pyrid-3-ylamine, pyrazolo[1,5-a]pyridine-3,5-diamine, 5-(morpholin-4-yl)pyrazolo[1,5-a]pyrid-3-ylamine, 2-[(3-aminopyrazolo[1,5-a]pyrid-5-yl)(2-hydroxyethyl)amino]ethanol, 2-[(3-aminopyrazolo[1,5-a]pyrid-7-yl)(2-hydroxyethyl)amino]ethanol, 3-aminopyrazolo[1,5-a]pyridin-5-ol, 3-aminopyrazolo[1,5-a]pyridin-4-ol, 3-aminopyrazolo[1,5-a]pyridin-6-ol and 3-aminopyrazolo[1,5-a]pyridin-7-ol, and addition salts thereof.

Among the pyrimidine derivatives that may be mentioned are the compounds described, for example, in patents DE 2359399, JP 88-169571, JP 05-63124 and EP 0 770 375 or patent application WO 96/15765, such as 2,4,5,6-tetraaminopyrimidine, 4-hydroxy-2,5,6-triaminopyrimidine, 2-hydroxy-4,5,6-triaminopyrimidine, 2,4-dihydroxy-5,6-diaminopyrimidine, 2,5,6-triaminopyrimidine and addition salts thereof, and tautomeric forms thereof, when a tautomeric equilibrium exists.

Among the pyrazole derivatives that may be mentioned are the compounds described in the patents DE 3843892, DE 4133957 and patent applications WO 94/08969, WO 94/08970, FR-A-2 733 749 and DE 195 43 988, such as 4,5-diamino-1-methylpyrazole, 4,5-diamino-1-( $\beta$ -hydroxyethyl)pyrazole, 3,4-diaminopyrazole, 4,5-diamino-1-(4'-chlorobenzyl)pyrazole, 4,5-diamino-1,3-dimethylpyrazole, 4,5-diamino-3-methyl-1-phenylpyrazole, 4,5-diamino-1-methyl-3-phenylpyrazole, 4-amino-1,3-dimethyl-5-hydrazinopyrazole, 1-benzyl-4,5-diamino-3-methylpyrazole, 4,5-diamino-3-tert-butyl-1-methylpyrazole, 4,5-diamino-1-tert-butyl-3-methylpyrazole, 4,5-diamino-1-( $\beta$ -hydroxyethyl)-3-methylpyrazole, 4,5-diamino-1-ethyl-3-methylpyrazole, 4,5-diamino-1-ethyl-3-(4'-methoxyphenyl)pyrazole, 4,5-diamino-1-ethyl-3-hydroxymethylpyrazole, 4,5-diamino-3-hydroxymethyl-1-methylpyrazole, 4,5-diamino-3-hydroxymethyl-1-isopropylpyrazole, 4,5-diamino-3-methyl-1-isopropylpyrazole, 4-amino-5-(2'-aminoethyl)amino-1,3-dimethylpyrazole, 3,4,5-triaminopyrazole, 1-methyl-3,4,5-triaminopyrazole, 3,5-diamino-1-methyl-4-methylaminopyrazole, 3,5-diamino-4-( $\beta$ -hydroxyethyl)amino-1-methylpyrazole, and the addition salts thereof. Use may also be made of 4,5-diamino-1-( $\beta$ -methoxyethyl)pyrazole.

Use will preferably be made of a 4,5-diaminopyrazole and more preferably still of 4,5-diamino-1-( $\beta$ -hydroxyethyl)pyrazole and/or a salt thereof.

Pyrazole derivatives that may also be mentioned include diamino-N,N-dihydropyrazolopyrazolones and especially those described in patent application FR-A-2 886 136, such as the following compounds and the addition salts thereof: 2,3-diamino-6,7-dihydro-1H,5H-pyrazolo[1,2-a]pyrazol-1-one, 2-amino-3-ethylamino-6,7-dihydro-1H,5H-pyrazolo[1,2-a]pyrazol-1-one, 2-amino-3-isopropylamino-6,7-dihydro-1H,5H-pyrazolo[1,2-a]pyrazol-1-one, 2-amino-3-(pyrrolidin-1-yl)-6,7-dihydro-1H,5H-pyrazolo[1,2-a]pyrazol-1-one, 4,5-diamino-1,2-dimethyl-1,2-dihydropyrazol-3-one,



4,5-diamino-1,2-diethyl-1,2-dihydropyrazol-3-one, 4,5-diamino-1,2-di(2-hydroxyethyl)-1,2-dihydropyrazol-3-one, 2-amino-3-(2-hydroxyethyl)amino-6,7-dihydro-1H,5H-pyrazolo[1,2-a]pyrazol-1-one, 2-amino-3-dimethylamino-6,7-dihydro-1H,5H-pyrazolo[1,2-a]pyrazol-1-one, 2,3-diamino-5,6,7,8-tetrahydro-1H,6H-pyridazino[1,2-a]pyrazol-1-one, 4-amino-1,2-diethyl-5-(pyrrolidin-1-yl)-1,2-dihydropyrazol-3-one, 4-amino-5-(3-dimethylaminopyrrolidin-1-yl)-1,2-diethyl-1,2-dihydropyrazol-3-one, 2,3-diamino-6-hydroxy-6,7-dihydro-1H,5H-pyrazolo[1,2-a]pyrazol-1-one. 2,3-Diamino-6,7-dihydro-1H,5H-pyrazolo[1,2-a]pyrazol-1-one and/or a salt thereof will preferably be used.

10 As heterocyclic bases, use will preferably be made of 4,5-diamino-1-( $\beta$ -hydroxyethyl)pyrazole and/or 2,3-diamino-6,7-dihydro-1H,5H-pyrazolo[1,2-a]pyrazol-1-one and/or a salt thereof.

Among the couplers that may be used in the composition of the invention, mention may be made especially of meta-phenylenediamines, meta-aminophenols, 15 meta-diphenols, naphthalene-based couplers and heterocyclic couplers, and also the addition salts thereof.

Mention may be made, for example, of 1,3-dihydroxybenzene, 1,3-dihydroxy-2-methylbenzene, 4-chloro-1,3-dihydroxybenzene, 2,4-diamino-1-( $\beta$ -hydroxyethyloxy)benzene, 2-amino-4-( $\beta$ -hydroxyethylamino)-1-methoxybenzene, 1,3-diaminobenzene, 1,3-bis(2,4-diaminophenoxy)propane, 3-ureidoaniline, 3-ureido-1-dimethylaminobenzene, sesamol, 1- $\beta$ -hydroxyethylamino-3,4-methylenedioxybenzene,  $\alpha$ -naphthol, 2-methyl-1-naphthol, 6-hydroxyindole, 4-hydroxyindole, 4-hydroxy-N-methylindole, 2-amino-3-hydroxypyridine, 6-hydroxybenzomorpholine, 3,5-diamino-2,6-dimethoxypyridine, 1-N-( $\beta$ -hydroxyethyl)amino-3,4-methylenedioxybenzene, 2,6-bis( $\beta$ -hydroxyethylamino)toluene, 6-hydroxyindoline, 2,6-dihydroxy-4-methylpyridine, 1-H-3-methylpyrazol-5-one, 1-phenyl-3-methylpyrazol-5-one, 2,6-dimethylpyrazolo[1,5-b]-1,2,4-triazole, 2,6-dimethyl[3,2-c]-1,2,4-triazole and 6-methylpyrazolo[1,5-a]benzimidazole, the addition salts thereof with an acid, and mixtures thereof.

30 The addition salts of the oxidation bases and couplers are especially chosen from the addition salts with an acid such as the hydrochlorides, hydrobromides, sulfates, citrates, succinates, tartrates, lactates, tosylates, benzenesulfonates, phosphates and acetates.

The oxidation base(s) are each generally present in an amount of from 0.0001% to 10% by weight relative to the total weight of the composition, and preferably from 35 0.005% to 5% by weight relative to the total weight of the composition.

The coupler(s) each generally represent from 0.0001% to 10% by weight relative to the total weight of the composition, and preferably from 0.005% to 5% by weight relative to the total weight of the composition.

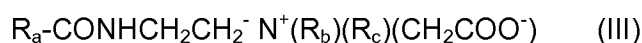
5 The composition according to the invention may contain synthetic or natural, cationic or nonionic, direct dyes.

Examples of particularly suitable direct dyes that may be mentioned include nitrobenzene dyes; azo direct dyes; azomethine direct dyes; methine direct dyes; azacarbocyanin direct dyes, for instance tetraazacarbocyanins (tetraazapentamethines); quinone and in particular anthraquinone, naphthoquinone or  
10 benzoquinone direct dyes; azine direct dyes; xanthene direct dyes; triarylmethane direct dyes; indoamine direct dyes; indigoid direct dyes; phthalocyanine direct dyes, porphyrin direct dyes and natural direct dyes, alone or as mixtures. In particular, mention may be made of direct dyes from among: azo; methine; carbonyl; azine; nitro (hetero)aryl; tri(hetero)arylmethane; porphyrin; phthalocyanine and natural direct  
15 dyes, alone or as mixtures.

When they are present, the direct dye(s) more particularly represent(s) from 0.0001% to 10% by weight and preferably from 0.005% to 5% by weight of the total weight of the composition.

The composition according to the invention comprises one or more surfactants.  
20 The surfactant(s) may be cationic, amphoteric, nonionic and/or anionic surfactants. The surfactants of use in the composition of the invention are surfactants known *per se* in the field of dyeing keratin fibres.

The amphoteric or zwitterionic surfactant(s) that may be used in the present invention may especially be optionally quaternized secondary or tertiary aliphatic  
25 amine derivatives, in which the aliphatic group is a linear or branched chain containing from 8 to 22 carbon atoms, the said amine derivatives containing at least one anionic group, for instance a carboxylate, sulfonate, sulfate, phosphate or phosphonate group. In particular, mention may be made of (C<sub>8</sub>-C<sub>20</sub>)alkylbetaines, sulfobetaines, (C<sub>8</sub>-C<sub>20</sub> alkyl)amido(C<sub>3</sub>-C<sub>8</sub> alkyl)betaines or (C<sub>8</sub>-C<sub>20</sub> alkyl)amido(C<sub>6</sub>-C<sub>8</sub>  
30 alkyl)sulfobetaines. Among the optionally quaternized, secondary or tertiary aliphatic amine derivatives that can be used, as defined above, mention may also be made of the compounds having the respective structures (III) and (III') below:



35

in which:

R<sub>a</sub> represents a C<sub>10</sub>-C<sub>30</sub> alkyl or alkenyl group derived from an acid,

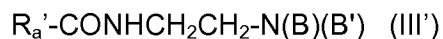
$R_a$ -COOH, preferably present in hydrolysed coconut oil, represents a heptyl, nonyl or undecyl group,

$R_b$  represents a  $\beta$ -hydroxyethyl group, and

$R_c$  represents a carboxymethyl group;

5

and



in which:

10

B represents  $-\text{CH}_2\text{CH}_2\text{OX}'$ ,

B' represents  $-(\text{CH}_2)_z-\text{Y}'$ , with  $z = 1$  or  $2$ ,

X' represents the group  $-\text{CH}_2-\text{COOH}$ ,  $\text{CH}_2-\text{COOZ}'$ ,  $-\text{CH}_2\text{CH}_2-\text{COOH}$ ,  $-\text{CH}_2\text{CH}_2-\text{COOZ}'$ , or a hydrogen atom,

Y' represents  $-\text{COOH}$ ,  $-\text{COOZ}'$ , the group  $-\text{CH}_2-\text{CHOH}-\text{SO}_3\text{H}$  or  $-\text{CH}_2-\text{CHOH}-\text{SO}_3\text{Z}'$ ,

15

Z' represents an ion derived from an alkali metal or alkaline-earth metal, such as sodium, an ammonium ion or an ion derived from an organic amine,

$R_a'$  represents a  $\text{C}_{10}$ - $\text{C}_{30}$  alkyl or alkenyl group of an acid  $R_a'-\text{COOH}$  preferably present in coconut oil or in hydrolysed linseed oil, an alkyl group, especially a  $\text{C}_{17}$  alkyl group, and its iso form, or an unsaturated  $\text{C}_{17}$  group.

20

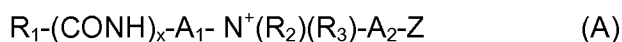
These compounds are classified in the CTFA dictionary, 5th edition, 1993, under the names disodium cocoamphodiacetate, disodium lauroamphodiacetate, disodium caprylamphodiacetate, disodium capryloamphodiacetate, disodium cocoamphodipropionate, disodium lauroamphodipropionate, disodium caprylamphodipropionate, disodium capryloamphodipropionate, lauroamphodipropionic acid and cocoamphodipropionic acid.

25

By way of example, mention may be made of the cocoamphodiacetate sold by the company Rhodia under the trade name Miranol<sup>®</sup> C2M Concentrate.

Among the amphoteric or zwitterionic surfactants mentioned above, use is preferably made of betaines comprising at least one saturated or unsaturated,  $\text{C}_8$ - $\text{C}_{30}$  fatty chain, and in particular the compounds of formula (A):

30



with

x denoting 0 or 1,

35

$\text{A}_1$  and  $\text{A}_2$  denoting, independently of one another, a linear or branched  $\text{C}_1$ - $\text{C}_{10}$  alkylene radical optionally substituted with a hydroxyl radical,

$\text{R}_1$  denoting a linear or branched  $\text{C}_6$ - $\text{C}_{30}$  alkyl or alkenyl radical,

$R_2$  and  $R_3$  denoting, independently of one another, a linear or branched  $C_1$ - $C_4$  alkyl radical,

$Z$  denoting a  $CO_2^-$  group or an  $SO_3^-$  group.

Preferably,  $R_2$  and  $R_3$  denote a methyl radical.

5       The amphoteric surfactant(s) of betaine type used in the cosmetic composition according to the present invention may especially be ( $C_{8-20}$ )alkylbetaines, ( $C_{8-20}$ )alkylsulfobetaines, ( $C_{8-20}$  alkyl)amido( $C_{2-8}$  alkyl)betaines or ( $C_{8-20}$  alkyl)amido( $C_{6-8}$  alkyl)sulfobetaines.

10       Among the amphoteric surfactants mentioned above that are preferably used are ( $C_{8-20}$  alkyl)betaines and ( $C_{8-20}$  alkyl)amido( $C_{2-8}$  alkyl)betaines, and mixtures thereof.

More particularly, the amphoteric surfactants of betaine type are selected from cocobetaine and cocamidopropylbetaine.

15       The term "anionic surfactant" means a surfactant comprising, as ionic or ionizable groups, only anionic groups. These anionic groups are preferably chosen from the following groups:  $CO_2H$ ,  $CO_2^-$ ,  $SO_3H$ ,  $SO_3^-$ ,  $OSO_3H$ ,  $OSO_3^-$ ,  $H_2PO_3$ ,  $HPO_3^-$ ,  $PO_3^{2-}$ ,  $H_2PO_2$ ,  $HPO_2$ ,  $HPO_2^-$ ,  $PO_2^-$ ,  $POH$ ,  $PO^-$ .

20       As examples of anionic surfactants that may be used in the composition according to the invention, mention may be made of alkyl sulfates, alkyl ether sulfates, alkylamido ether sulfates, alkylaryl polyether sulfates, monoglyceride sulfates, alkyl sulfonates, alkylamide sulfonates, alkylaryl sulfonates, alpha-olefin sulfonates, paraffin sulfonates, alkyl sulfosuccinates, alkyl ether sulfosuccinates, alkylamide sulfosuccinates, alkyl sulfoacetates, acyl sarcosinates, acyl glutamates, alkyl sulfosuccinamates, acyl isethionates and N-acyltaurates, salts of alkyl  
25       monoesters of polyglycoside-polycarboxylic acids, acyl lactylates, D-galactoside-uronic acid salts, alkyl ether carboxylic acid salts, alkylaryl ether carboxylic acid salts, alkylamido ether carboxylic acid salts; and the corresponding non-salified forms of all these compounds; the alkyl and acyl groups of all these compounds comprising from 6 to 24 carbon atoms and the aryl group denoting a phenyl group.

30       These compounds may be oxyethylenated and then preferably comprise from 1 to 50 ethylene oxide units.

The salts of  $C_6$ - $C_{24}$  alkyl monoesters of polyglycoside-polycarboxylic acids may be chosen from  $C_6$ - $C_{24}$  alkyl polyglycoside citrates,  $C_6$ - $C_{24}$  alkyl polyglycoside tartrates and  $C_6$ - $C_{24}$  alkyl polyglycoside sulfosuccinates.

35       When the anionic surfactant(s) are in salt form, they may be chosen from alkali metal salts such as the sodium or potassium salt and preferably the sodium

salt, the ammonium salts, the amine salts and in particular the amino alcohol salts or the alkaline-earth metal salts such as the magnesium salt.

Examples of amino alcohol salts that may especially be mentioned include monoethanolamine, diethanolamine and triethanolamine salts,  
 5 monoisopropanolamine, diisopropanolamine or triisopropanolamine salts, 2-amino-2-methyl-1-propanol salts, 2-amino-2-methyl-1,3-propanediol salts and tris(hydroxymethyl)aminomethane salts.

Alkali metal or alkaline-earth metal salts and in particular the sodium or magnesium salts are preferably used.

10 Among the anionic surfactants, it is preferred, according to the invention, to use alkyl sulfate salts and alkyl ether sulfate salts and mixtures thereof.

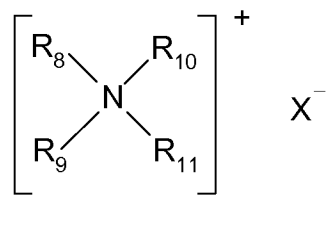
The term "cationic surfactant" means a surfactant that is positively charged when it is contained in the composition according to the invention. This surfactant may bear one or more positive permanent charges or may contain one  
 15 or more cationizable functions within the composition according to the invention.

The cationic surfactant(s) that may be used according to the present invention are preferably chosen from optionally polyoxyalkylenated primary, secondary or tertiary fatty amines, or the salts thereof, quaternary ammonium salts, and mixtures thereof.

20 The fatty amines generally comprise at least one C<sub>8</sub>-C<sub>30</sub> hydrocarbon-based chain. Among the fatty amines that can be used according to the invention, examples that may be mentioned include stearylamidopropyldimethylamine and distearylamine.

Examples of quaternary ammonium salts that may especially be  
 25 mentioned include:

- those corresponding to the general formula (IV) below:

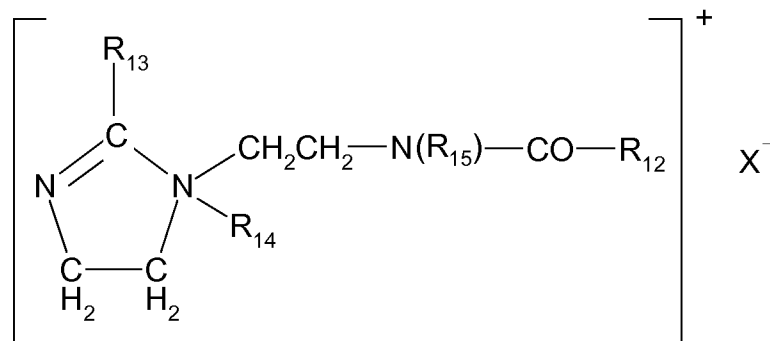


in which the groups R<sub>8</sub> to R<sub>11</sub>, which may be identical or different, represent a linear or branched aliphatic group containing from 1 to 30 carbon  
 30 atoms, or an aromatic group such as aryl or alkylaryl, at least one of the groups R<sub>8</sub> to R<sub>11</sub> denoting a group containing from 8 to 30 carbon atoms, preferably from 12 to 24 carbon atoms. The aliphatic groups may comprise heteroatoms such as, in

particular, oxygen, nitrogen, sulfur and halogens. The aliphatic groups are chosen, for example, from C<sub>1-30</sub> alkyl, C<sub>1-30</sub> alkoxy, polyoxy(C<sub>2</sub>-C<sub>6</sub>)alkylene, C<sub>1-30</sub> alkylamide, (C<sub>12</sub>-C<sub>22</sub>)alkylamido(C<sub>2</sub>-C<sub>6</sub>)alkyl, (C<sub>12</sub>-C<sub>22</sub>)alkylacetate and C<sub>1-30</sub> hydroxyalkyl; X<sup>-</sup> is an anion chosen from the group of halides, phosphates, acetates, lactates, (C<sub>1</sub>-C<sub>4</sub>)alkyl sulfates, and (C<sub>1</sub>-C<sub>4</sub>)alkyl- or (C<sub>1</sub>-C<sub>4</sub>)alkylaryl- sulfonates.

Among the quaternary ammonium salts of formula (IV), those that are preferred are, on the one hand, tetraalkylammonium salts, for instance dialkyldimethylammonium or alkyltrimethylammonium salts in which the alkyl group contains approximately from 12 to 22 carbon atoms, in particular behenyltrimethylammonium, distearyldimethylammonium, cetyltrimethylammonium or benzyldimethylstearylammonium salts, or, on the other hand, the palmitylamidopropyltrimethylammonium salt, the stearamidopropyltrimethylammonium salt, the stearamidopropyldimethylcetearylammonium salt, or the stearamidopropyldimethyl(myristyl acetate)ammonium salt sold under the name Ceraphyl® 70 by the company Van Dyk. It is particularly preferred to use the chloride salts of these compounds;

- quaternary ammonium salts of imidazoline, for instance those of formula (V) below:



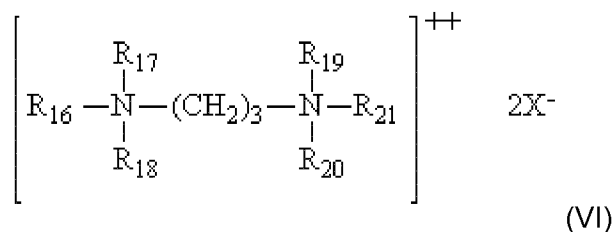
(V)

in which R<sub>12</sub> represents an alkyl or alkenyl group containing from 8 to 30 carbon atoms, derived for example from tallow fatty acids, R<sub>13</sub> represents a hydrogen atom, a C<sub>1</sub>-C<sub>4</sub> alkyl group or an alkyl or alkenyl group containing from 8 to 30 carbon atoms, R<sub>14</sub> represents a C<sub>1</sub>-C<sub>4</sub> alkyl group, R<sub>15</sub> represents a hydrogen atom or a C<sub>1</sub>-C<sub>4</sub> alkyl group, X<sup>-</sup> is an anion selected from the group consisting of halides, phosphates, acetates, lactates, alkyl sulfates, alkylsulfonates or alkylarylsulfonates in which the alkyl and aryl groups each preferably comprise from 1 to 20 carbon atoms and from 6 to 30 carbon atoms. R<sub>12</sub> and R<sub>13</sub> preferably denote a mixture of alkyl or alkenyl groups comprising from 12 to 21 carbon atoms,

for example tallow fatty acid derivatives,  $R_{14}$  denotes a methyl group, and  $R_{15}$  denotes a hydrogen atom. Such a product is sold, for example, under the name Rewoquat® W 75 by the company Rewo;

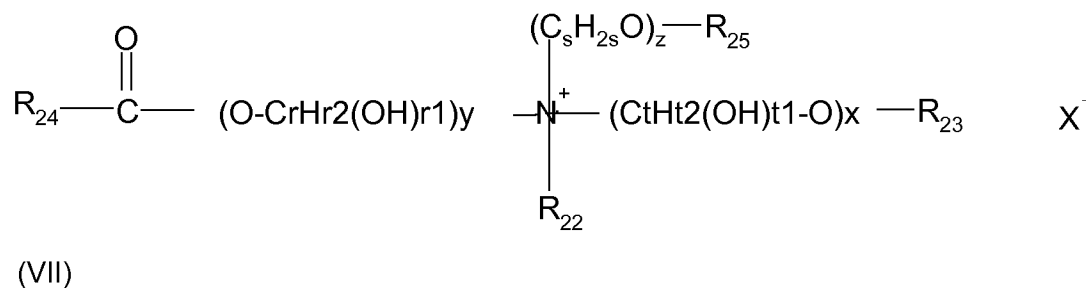
- quaternary diammonium or triammonium salts, in particular of formula

5 (VI):



in which  $R_{16}$  denotes an alkyl radical containing approximately from 16 to 30 carbon atoms, which is optionally hydroxylated and/or interrupted by one or more oxygen atoms,  $R_{17}$  is selected from hydrogen and an alkyl radical containing from 1 to 4 carbon atoms or a group  $(R_{16a})(R_{17a})(R_{18a})N-(CH_2)_3$ ,  $R_{16a}$ ,  $R_{17a}$ ,  $R_{18a}$ ,  $R_{18}$ ,  $R_{19}$ ,  $R_{20}$  and  $R_{21}$ , which are identical or different, are selected from hydrogen and an alkyl radical containing from 1 to 4 carbon atoms, and  $X^-$  is an anion selected from the group of halides, acetates, phosphates, nitrates and methyl sulfates. Such compounds are, for example, Finquat CT-P, available from the company Finetex (Quaternium 89), and Finquat CT, available from the company Finetex (Quaternium 75),

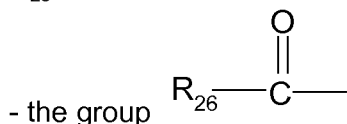
- quaternary ammonium salts containing at least one ester function, such as those of formula (VII) below:



in which:

$R_{22}$  is selected from  $C_1$ - $C_6$  alkyl groups and  $C_1$ - $C_6$  hydroxyalkyl or dihydroxyalkyl groups;

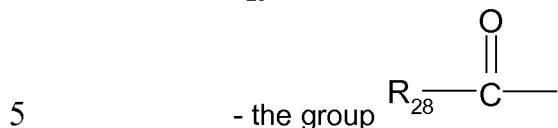
25  $R_{23}$  is selected from:



- groups  $R_{27}$ , which are linear or branched, saturated or unsaturated  $C_1$ - $C_{22}$  hydrocarbon-based groups,

- a hydrogen atom,

$R_{25}$  is selected from:



- groups  $R_{29}$ , which are linear or branched, saturated or unsaturated  $C_1$ - $C_6$  hydrocarbon-based groups,

- a hydrogen atom,

10                     $R_{24}$ ,  $R_{26}$  and  $R_{28}$ , which are identical or different, are selected from linear or branched, saturated or unsaturated  $C_7$ - $C_{21}$  hydrocarbon radicals;

$r$ ,  $s$  and  $t$ , which may be identical or different, are integers ranging from 2 to 6;

$r_1$  and  $t_1$ , which may be identical or different, are equal to 0 or 1,

and  $r_2+r_1=2r$  and  $t_1+t_2=2t$ ,

15

$y$  is an integer ranging from 1 to 10;

$x$  and  $z$ , which may be identical or different, are integers ranging from 0 to 10;

$X^-$  is a simple or complex, organic or inorganic anion;

20

with the proviso that the sum  $x + y + z$  is from 1 to 15, that when  $x$  is 0, then  $R_{23}$  denotes  $R_{27}$  and that when  $z$  is 0, then  $R_{25}$  denotes  $R_{29}$ .

The alkyl groups  $R_{22}$  may be linear or branched, and more particularly linear.

25                    Preferably,  $R_{22}$  denotes a methyl, ethyl, hydroxyethyl or dihydroxypropyl group, and more particularly a methyl or ethyl group.

Advantageously, the sum  $x + y + z$  is from 1 to 10.

When  $R_{23}$  is a hydrocarbon-based group  $R_{27}$ , it may be long and may have 12 to 22 carbon atoms, or may be short and may have from 1 to 3 carbon atoms.

30

When  $R_{25}$  is a hydrocarbon-based group  $R_{29}$ , it preferably contains 1 to 3 carbon atoms.

Advantageously,  $R_{24}$ ,  $R_{26}$  and  $R_{28}$ , which may be identical or different, are chosen from linear or branched, saturated or unsaturated  $C_{11}$ - $C_{21}$  hydrocarbon-based groups, and more particularly from linear or branched, saturated or  
35                    unsaturated  $C_{11}$ - $C_{21}$  alkyl and alkenyl groups.



Preferably, x and z, which may be identical or different, are equal to 0 or 1.

y is advantageously equal to 1.

Preferably, r, s and t, which may be identical or different, equal 2 or 3, and even more particularly are equal to 2.

The anion  $X^-$  is preferably a halide (chloride, bromide or iodide) or an alkyl sulfate, more particularly methyl sulfate. However, it is possible to use methanesulfonate, phosphate, nitrate, tosylate, an anion derived from an organic acid, such as acetate or lactate, or any other anion that is compatible with the ammonium containing an ester function.

The anion  $X^-$  is even more particularly chloride or methyl sulfate.

Use is made more particularly, in the composition according to the invention, of the ammonium salts of formula (VII) in which:

$R^{22}$  denotes a methyl or ethyl group,

x and y are equal to 1;

z is equal to 0 or 1;

r, s and t are equal to 2;

$R_{23}$  is selected from:

- the group  $R_{26}-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-$

- methyl, ethyl or  $C_{14}$ - $C_{22}$  hydrocarbon-based groups,

- a hydrogen atom,

$R_{25}$  is selected from:

- the group  $R_{28}-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-$

- a hydrogen atom,

$R_{24}$ ,  $R_{26}$  and  $R_{28}$ , which may be identical or different, are chosen from linear or branched, saturated or unsaturated  $C_{13}$ - $C_{17}$  hydrocarbon-based groups, and preferably from linear or branched, saturated or unsaturated  $C_{13}$ - $C_{17}$  alkyl and alkenyl groups.

The hydrocarbon-based groups are advantageously linear.

Mention may be made, for example, of the compounds of formula (VII) such as the diacyloxyethyldimethylammonium, diacyloxyethylhydroxyethylmethylammonium, monoacyloxyethyldihydroxyethylmethylammonium,

triacyloxyethylmethylammonium and  
monoacyloxyethylhydroxyethylmethylammonium salts (chloride or methyl sulfate  
in particular), and mixtures thereof. The acyl groups preferably contain 14 to 18  
carbon atoms and are obtained more particularly from a plant oil such as palm oil  
or sunflower oil. When the compound contains several acyl groups, these groups  
may be identical or different.

These products are obtained, for example, by direct esterification of  
triethanolamine, of triisopropanolamine, of an alkyldiethanolamine or of an  
alkyldiisopropanolamine, which are optionally oxyalkylenated, with C<sub>10</sub>-C<sub>30</sub> fatty  
acids or with mixtures of C<sub>10</sub>-C<sub>30</sub> fatty acids of plant or animal origin, or by  
transesterification of the methyl esters thereof. This esterification is followed by a  
quaternization using an alkylating agent such as an alkyl halide (preferably a  
methyl or ethyl halide), a dialkyl sulfate (preferably a dimethyl or diethyl sulfate),  
methyl methanesulfonate, methyl para-toluenesulfonate, glycol chlorohydrin or  
glycerol chlorohydrin.

Such compounds are sold, for example, under the names Dehyquart® by  
the company Henkel, Stepanquat® by the company Stepan, Noxamium® by the  
company Ceca or Rewoquat® WE 18 by the company Rewo-Witco.

The composition according to the invention may contain, for example, a  
mixture of quaternary ammonium monoester, diester and triester salts with a  
weight majority of diester salts.

It is also possible to use the ammonium salts containing at least one ester  
function that are described in patents US-A-4 874 554 and US-A-4 137 180.

Use may be made of behenoylhydroxypropyltrimethylammonium chloride  
sold by KAO under the name Quatarmin BTC 131.

Preferably, the ammonium salts containing at least one ester function  
contain two ester functions.

Among the quaternary ammonium salts containing at least one ester  
function, which can be used, it is preferred to use  
dipalmitoylethylhydroxyethylmethylammonium salts.

The nonionic surfactants are more particularly chosen from mono-  
oxyalkylenated or polyoxyalkylenated and monoglycerolated or polyglycerolated  
nonionic surfactants. The oxyalkylene units are more particularly oxyethylene or  
oxypropylene units, or a combination thereof, preferably oxyethylene units.

Examples of oxyalkylenated nonionic surfactants that may be mentioned  
include:

- oxyalkylenated (C<sub>8</sub>-C<sub>24</sub>)alkylphenols,

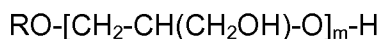
- saturated or unsaturated, linear or branched, oxyalkylenated C<sub>8</sub>-C<sub>30</sub> alcohols,
- saturated or unsaturated, linear or branched, oxyalkylenated C<sub>8</sub>-C<sub>30</sub> amides,
- esters of saturated or unsaturated, linear or branched, C<sub>8</sub>-C<sub>30</sub> acids and of polyethylene glycols,
- 5 • polyoxyethylenated esters of saturated or unsaturated, linear or branched, C<sub>8</sub>-C<sub>30</sub> acids and of sorbitol,
- saturated or unsaturated, oxyethylenated plant oils,
- the condensates of ethylene oxide and/or of propylene oxide, inter alia, alone or as mixtures.

10 The surfactants contain a number of moles of ethylene oxide and/or of propylene oxide of between 1 and 100, preferably between 2 and 50 and preferably between 2 and 30.

In accordance with one preferred embodiment of the invention, the oxyalkylenated nonionic surfactants are chosen from oxyethylenated C<sub>8</sub>-C<sub>30</sub> alcohols comprising from 1 to 100 mol of ethylene oxide; polyoxyethylenated esters of linear or  
15 branched, saturated or unsaturated C<sub>8</sub>-C<sub>30</sub> acids and of sorbitol comprising from 1 to 100 mol of ethylene oxide.

As examples of monoglycerolated or polyglycerolated nonionic surfactants, monoglycerolated or polyglycerolated C<sub>8</sub>-C<sub>40</sub> alcohols are preferably used.

20 In particular, the monoglycerolated or polyglycerolated C<sub>8</sub>-C<sub>40</sub> alcohols correspond to the following formula:



in which R represents a linear or branched C<sub>8</sub>-C<sub>40</sub> and preferably C<sub>8</sub>-C<sub>30</sub> alkyl or alkenyl radical, and m represents a number ranging from 1 to 30 and preferably from  
25 1 to 10.

As examples of compounds that are suitable in the context of the invention, mention may be made of lauryl alcohol containing 4 mol of glycerol (INCI name: Polyglyceryl-4 Lauryl Ether), lauryl alcohol containing 1.5 mol of glycerol, oleyl alcohol containing 4 mol of glycerol (INCI name: Polyglyceryl-4 Oleyl Ether), oleyl alcohol containing 2 mol of glycerol (INCI name: Polyglyceryl-2 Oleyl Ether), cetearyl alcohol containing 2 mol of glycerol, cetearyl alcohol containing 6 mol of glycerol, oleyl/cetyl alcohol containing 6 mol of glycerol, and octadecanol containing 6 mol of glycerol.

The alcohol may represent a mixture of alcohols in the same way that the value of m represents a statistical value, which means that, in a commercial product,  
35 several species of polyglycerolated fatty alcohols may coexist in the form of a mixture.

Among the monoglycerolated or polyglycerolated alcohols, it is more particularly preferred to use the C<sub>8</sub>/C<sub>10</sub> alcohol containing 1 mol of glycerol, the C<sub>10</sub>/C<sub>12</sub> alcohol containing 1 mol of glycerol and the C<sub>12</sub> alcohol containing 1.5 mol of glycerol.

Nonionic surfactants that may also be mentioned include non-oxyethylenated fatty acid esters of sorbitan, fatty acid esters of sucrose, optionally oxyalkylenated alkylpolyglycosides, alkylglucoside esters, derivatives of N-alkylglucamine and of N-acylmethylglucamine, aldobionamides and amine oxides.

5 According to one embodiment of the invention, the composition comprises one or more nonionic or anionic surfactants. Preferentially, the composition of the invention comprises one or more nonionic surfactants.

The total content of surfactants in the composition of the invention is in general from 0.1% to 30% by weight, preferably from 1% to 20% by weight and better still  
10 from 2% to 10% by weight, relative to the weight of the composition.

The composition may also contain various adjuvants conventionally used in compositions for dyeing or lightening the hair, such as anionic polymers, cationic polymers, and nonionic polymers, or mixtures thereof; antioxidants; penetrants; sequestrants; fragrances; dispersants; film-forming agents; ceramides; preserving  
15 agents; opacifiers.

The above adjuvants are generally present in an amount for each of them of between 0.01% and 20% by weight relative to the weight of the composition.

Preferentially, the composition according to the invention comprises one or more cationic polymers.

20 The composition according to the invention may comprise water and/or one or more organic solvents other than the diols of the invention.

Examples of organic solvents that may be mentioned include monoalcohols, such as ethanol or isopropanol; aromatic alcohols such as benzyl alcohol or phenylethyl alcohol; polyols other than the diols of the invention, such as glycerol or  
25 propylene glycol; polyol ethers, for instance ethylene glycol monomethyl, monoethyl or monobutyl ether, propylene glycol ethers, for instance propylene glycol monomethyl ether; and also diethylene glycol alkyl ethers, especially C<sub>1</sub>-C<sub>4</sub> alkyl ethers, for instance diethylene glycol monoethyl ether or monobutyl ether, alone or as a mixture.

30 The organic solvents other than the diols of the invention, when they are present, generally represent between 1% and 40% by weight relative to the total weight of the dye composition, and preferably between 5% and 30% by weight relative to the total weight of the dye composition.

The composition is preferably aqueous. In this case, it preferably comprises  
35 from 30% to 95% by weight of water, better still from 40% to 90% by weight of water and even better still from 50% to 85% by weight of water relative to the total weight of the composition.

The pH of the composition according to the invention, if it is aqueous, is generally between 3 and 12, preferably between 5 and 11 and preferentially between 7 and 11, limits inclusive.

It may be adjusted to the desired value by means of acidifying or basifying agents usually used in the dyeing of keratin fibres, and in particular the  
5      aforementioned alkaline agents of the invention.

The composition, before dispersing in the form of a foam, may result from the mixing of two or more than two compositions.

The composition according to the invention is, on application to the keratin  
10      fibres, in the form of a foam.

The composition in foam form according to the invention is formed from a mixture of air or an inert gas with the composition described previously.

According to one particularly preferred embodiment, the composition according to the invention is in the form of a temporary foam produced just before  
15      use.

The composition may be packaged in a foam dispenser. They may either be products known as "aerosols" dispensed from a pressurized container with the aid of a propellant gas and thus forming a foam at the moment they are dispensed, or compositions dispensed from a container using a mechanical pump connected to a  
20      dispensing head, the passage of the composition into the dispensing head converting it into a foam at the latest at the outlet orifice of such a head.

The propellant gas that may be used may be chosen from carbon dioxide, nitrogen, nitrogen oxide, dimethyl ether, volatile hydrocarbons such as butane, isobutane, propane and pentane, and mixtures thereof.

According to another embodiment, the composition may be in a foam  
25      dispenser of "pump-action bottle" type. These dispensers comprise a dispensing head for delivering the composition, a pump and a dip tube for transferring the composition from the container into the head in order to deliver the product. The foam is formed by forcing the composition to pass through a material comprising a porous substance  
30      such as a sintered material, a filtering grid made of plastic or of metal, or similar structures.

Such dispensers are well known to those skilled in the art and are described in patents: U.S. Pat No. 3 709 437 (Wright), U.S. Pat. No. 3 937 364 (Wright), U.S. Pat No. 4 022 351 (Wright), U.S. Pat No. 4 147 306 (Bennett), U.S. Pat  
35      No. 4 184 615 (Wright), U.S. Pat No. 4 598 862 (Rice), U.S. Pat No. 4 615 467 (Grogan et al.), and U.S. Pat No. 5 364 031 (Tamiguchi et al.).

In practice, for this variant, the oxidizing agent(s) are packaged in a first container equipped with a closure, and the oxidation dye precursor(s) are packaged in a second container, different from the first, and also closed by a closing member. The closing member may be a pump-dispensing mechanism. The composition according to the invention is then formed by mixing, before use, a composition with the oxidizing agent(s) and a composition with the oxidation dye precursor(s). To this end, to limit the number of containers provided, one from among the first and second container defines an internal volume that is sufficient to receive therein all of the two compositions. The mixture of the compositions may be homogenized by closing this container and by shaking the container. The closure of the container is advantageously carried out directly with the dispensing head. This dispensing head comprises a mechanical pump held in a ring intended for mounting by snap-fitting or screwing onto the neck of the container containing the mixture. The pump comprises a pump body connected to a dip tube to enable the whole of the mixture to be dispensed. The pump also comprises a push button for activation of the pump body, such that, on each activation, a dose of composition is sucked inside the dip tube and ejected in foam form out of the dispensing orifice of the head.

The containers are preferentially made of a thermoplastic material, and obtained via extrusion blow-moulding or injection blow-moulding processes. In particular, the container for conditioning the composition with the oxidation dye precursor(s) may be (to be reported in other projects) made of a material comprising a non-zero proportion of EVOH. The pump is, for example, the standard "F2 - L9" model offered by the company Rexam.

According to this preferred embodiment, one subject of the invention is a non-aerosol device comprising the composition of the invention in liquid form.

The dyeing process according to the invention consists in applying the composition according to the invention to wet or dry keratin fibres over a time sufficient to develop the desired coloration. According to the invention, the composition applied to the keratin fibres is in foam form. The dyeing process is generally performed at room temperature (between 15 and 25°C) and up to temperatures that may be as high as 60°C to 80°C.

After a leave-on time of from one minute to one hour and preferably from 5 minutes to 30 minutes, the human keratin fibres are rinsed with water, and optionally washed with a shampoo and then rinsed with water.

The examples that follow serve to illustrate the invention without, however, being limiting in nature.

**EXAMPLES**

The following compositions are prepared (the amounts are expressed in g% of active material):

Ingredients	Amount (g)
Ammonium thiolactate	0.2
Aqueous ammonia (expressed as NH <sub>3</sub> )	0.8
Erythorbic acid	0.1
Monoethanolamine	2
Ethylenediaminetetraacetic acid	0.1
Oleyl alcohol	0.5
Fragrance	0.4
Polydimethyldiallylammonium chloride (Polyquaternium-6)	0.5
Hexylene glycol (2-methyl-2,4-pentanediol)	2
Dipropylene glycol	2
96° ethyl alcohol	3
Propylene glycol	2
Oxyethylenated decyl alcohol (3 OE)	4
Protected oxyethylenated (4 OE) rapeseed acid amide (INCI: PEG-4 rapeseed amide)	3
Lauryl ether carboxylic acid (4.5 OE)	2
Glyceryl C12 alkyl ether (1.5 mol) (INCI: glyceryl lauryl ether)	3
Condensate of ethylene oxide and of propylene oxide and ethylene oxide (MW: 14000) (128 OE/54 OP/128 OE) (INCI: Poloxamer 338)	1
Hydrogen peroxide	4.5
Phosphoric acid	qs
Etidronic acid, tetrasodium salt	0.04
Tetrasodium pyrophosphate	0.02
Sodium salicylate	0.02

Glycerol	2
Laureth-11	1
1,4-Diaminobenzene	0.8
1- $\beta$ -Hydroxyethyloxy-2,4-diaminobenzene dihydrochloride	0.04
1N,N-Bis(2-hydroxyethyl)amino-4-aminobenzene sulfate monohydrate	0.18
2-Methyl-1,3-dihydroxybenzene	0.028
1,3-Dihydroxybenzene	0.68
1-Hydroxy-3-aminobenzene	0.24
Water	qs 100

The above dye composition is obtained by mixing, before use, the following two compositions in a composition A/composition B weight ratio of 0.666.

5

<b>Composition A</b>	<b>% by weight</b>
Ammonium thiolactate	0.5
Aqueous ammonia (expressed as NH <sub>3</sub> )	2
Erythorbic acid	0.25
Monoethanolamine	5
Ethylenediaminetetraacetic acid	0.25
Oleyl alcohol	1.25
Fragrance	1
Polydimethyldiallylammonium chloride (Polyquaternium-6)	1.25
Hexylene glycol (2-methyl-2,4-pentanediol)	5
Dipropylene glycol	5
96° ethyl alcohol	7.5
Propylene glycol	5
Oxyethylenated decyl alcohol (3 OE)	10
Protected oxyethylenated (4 OE) rapeseed acid amide (INCI: PEG-4 rapeseed amide)	7.5
Lauryl ether carboxylic acid (4.5 OE)	5
Glyceryl C12 alkyl ether (1.5 mol) (INCI: glyceryl lauryl ether)	7.5
Condensate of ethylene oxide and of propylene oxide and ethylene oxide (MW: 14000) (128 OE/54 OP/128 OE) (INCI: Poloxamer 338)	2.5
1,4-Diaminobenzene	2
1- $\beta$ -Hydroxyethyloxy-2,4-diaminobenzene dihydrochloride	0.1
1N,N-Bis(2-hydroxyethyl)amino-4-aminobenzene	0.45



sulfate monohydrate	
2-Methyl-1,3-dihydroxybenzene	0.07
1,3-Dihydroxybenzene	1.7
1-Hydroxy-3-aminobenzene	0.6
Water	qs 100

Composition B	% by weight
Glycerol	4
Etidronic acid, tetrasodium salt	0.06
Tetrasodium pyrophosphate	0.04
Sodium salicylate	0.035
Hydrogen peroxide	7.5
Laureth-11	1
Phosphoric acid	qs pH 2.2
Water	qs 100

5 The mixture is introduced in an amount of 65 g (26 g of composition A + 39 g of composition B) into a pump bottle (Rexam L9 equipped with a dip tube). The device produces a sufficiently compact foam on pumping. This foam is applied to natural or permanent-waved grey hair containing 90% white hairs, without disintegrating immediately on application.

10 The comfort on application is very good. After a leave-in time of 30 minutes, the locks are rinsed, washed with a standard shampoo, rinsed again and then dried, to give a dark chestnut-brown coloration. This coloration is strong and sparingly selective.

## CLAIMS

1. Dye composition in foam form comprising at least one oxidation dye precursor, at least one oxidizing agent, at least one alkaline agent and at least two diol compounds comprising at least 4 carbon atoms selected from dipropylene glycol, diethylene glycol and hexylene glycol.  
5
2. Composition according to the preceding claim, characterized in that it comprises as oxidation dye precursors one or more oxidation bases chosen from para-phenylenediamines, bis(phenyl)alkylenediamines, para-aminophenols, ortho-aminophenols and heterocyclic bases, and the addition salts thereof, and optionally one or more couplers chosen from meta-phenylenediamines, meta-aminophenols, meta-diphenols, naphthalene-based couplers and heterocyclic couplers, and also the addition salts thereof.  
10
3. Composition according to either of the preceding claims, in which the oxidizing agent is hydrogen peroxide.  
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4. Composition according to any one of the preceding claims, in which the alkaline agent is chosen from mineral alkaline agents and organic alkaline agents.  
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5. Composition according to any one of the preceding claims, in which the alkaline agent(s) are chosen from ammonia and monoethanolamine, and mixtures thereof.  
25
6. Composition according to any one of the preceding claims, in which the two diol compounds are dipropylene glycol and hexylene glycol.
- 30 7. Composition according to any one of the preceding claims, in which the amount of diol compounds ranges from 0.1% to 30%, preferably from 0.5% to 20% and better still from 1% to 10% by weight relative to the total weight of the composition.
- 35 8. Composition according to any one of the preceding claims, additionally comprising at least one surfactant, preferably a nonionic surfactant.
9. Hair dyeing process, characterized in that a composition comprising at least one dye precursor, at least one alkaline agent and at least two diol compounds comprising at least 4 carbon atoms selected from dipropylene glycol, diethylene  
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glycol and hexylene glycol is mixed with an oxidizing agent, and the mixture is then applied in foam form onto the hair; the dye precursor, the alkaline agent, the diol compounds and the oxidizing agent being as defined in any one of Claims 1 to 8.

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**10.** Aerosol device comprising a means for generating in foam form a composition as defined in any one of Claims 1 to 8.

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**11.** Non-aerosol device comprising a bottle equipped with a mechanical pumping system and comprising a composition as defined in any one of Claims 1 to 8 in liquid form and a dispensing system for delivering it in foam form.

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**12.** Multi-compartment device comprising, in a first compartment, a first composition containing at least one oxidation dye precursor, at least one alkaline agent and at least two diol compounds each comprising at least 4 carbon atoms selected from dipropylene glycol, diethylene glycol and hexylene glycol; in a second compartment, a second composition containing one or more oxidizing agents, one of the two compartments being equipped with a component for delivering the composition of the invention in foam form after mixing with the other composition, or the component for delivering the composition in foam form is included in a third compartment; the dye precursor, the alkaline agent, the diol compounds and the oxidizing agent being as defined in any one of Claims 1 to 8.

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# INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2012/069212

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> INV. A61K8/04      A61K8/34      A61Q5/10 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) A61K A61Q		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data, CHEM ABS Data		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2011/075657 A2 (PROCTER & GAMBLE [US]; LANE BRANDON SCOTT [US]; VOHRA FIROJ [US]; GALA) 23 June 2011 (2011-06-23) page 2, paragraph 5 - page 3, paragraph 1; claims; examples B-E; tables 3,3 page 9, line 3 - page 10, line 3 page 12, line 22 - page 31, line 18; figures 1,3	11
Y	----- DATABASE GNPD [Online] Mintel; 1 October 2010 (2010-10-01), "Hair color", XP055029153, Database accession no. 1422757 Ingredients, Product description ----- <div style="text-align: right;">-/-</div>	1-9
<div style="display: flex; justify-content: space-between;"> <span><input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C.</span> <span><input checked="" type="checkbox"/> See patent family annex.</span> </div>		
<div style="display: flex;"> <div style="flex: 1;"> <p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="flex: 1;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search  <div style="text-align: center; font-size: 1.2em;">26 November 2012</div>		Date of mailing of the international search report  <div style="text-align: center; font-size: 1.2em;">06/12/2012</div>
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer  <div style="text-align: center; font-size: 1.2em;">Loloiu, Teodora</div>

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2012/069212

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	<p>US 2004/068805 A1 (FISHMAN YORAM [US])  15 April 2004 (2004-04-15)  paragraph [0006] - paragraph [0008]  paragraph [0014] - paragraph [0018]  paragraph [0022] - paragraph [0028];  claims; tables 1-4</p> <p>-----</p>	1-10,12
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A	<p>FR 2 156 527 A1 (BRISTOL MYERS CO BRISTOL MYERS CO [US]) 1 June 1973 (1973-06-01)  page 26, line 33 - page 28, line 5;  example 17  page 10, line 23 - page 15, line 26</p> <p>-----</p>	1-12
A	<p>US 2008/256724 A1 (BOLTON PHILIP DAVID [GB] ET AL) 23 October 2008 (2008-10-23)  paragraph [0013] - paragraph [0077];  examples</p> <p>-----</p>	1-12

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International application No

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